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TITLE OPTICAL MEASUREMENTS OF SURFACE OXIDE LAYER FORMATION ON METAL FILMS

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Optical Measurements of Surface Oxide Layer Formation on Metal Films

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We have employed two optical techniques which give complementary indications of the formation of monolayers of oxide on freshly evaporated aluminum and silicon thin films. Visible ellipsometry is utilized to observe the growth of the initial monolayer of oxide on these films. From these data, we deduce the pressure and coverage dependence as well as the growth rate for the initial monolayer arising from these surface reactions. In addition, extreme ultraviolet (XUV) reflectance vs angle of incidence measurements at 58.4 nm wavelength clearly indicate the growth of oxide on the surface of our freshly deposited aluminum and silicon films as well. We have utilized this reflectance data to deduce the optical constants of aluminum and silicon at 58.4 nm. We find that previous XUV measurements of these optical constants were hampered by the presence of oxides. We also determined that the XUV reflectivity performance of aluminum films freshly deposited in our UHV system does not degrade appreciably when stored for four weeks in a helium atmosphere of 2 x 10 ³ Torr.

Key words: aluminum; ellipsometry; oxidation; reflectance; silicon; UHV films; XUV.

1. Introduction

Applications for XUV grazing incidence reflectors range from resonator mirrors for an XUV free-electron laser to imaging optics for XUV photolithography and synchrotron optics [1,2]. These applications can take advantage of the total-external-reflectance (TER) which occurs for aluminum and silicon in the extreme ultraviolet (XUV). The performance of these grazing incidence reflectors can be significantly degraded by the presence of oxide surface layers that form on the thin film reflectors when they are exposed to the atmosphere [3-8]. We have undertaken a study of the formation of surface oxide layers that form on aluminum and silicon thin films deposited in our ultra-high vacuum (UHV) deposition system [9]. We utilize in situ visible ellipsometry to observe the time evolution of the surface oxidation and in situ XUV reflectometry to determine material optical constants and the loss of XUV reflectance from the oxidized surface.

2. UHV Deposition and Analysis Chamber

Our UHV chamber is capable of a base pressure of 2×10^{-10} Torr when it is fully baked at 200°C for 24-48 hours. The pumps on the system are oil-free (sorption/ion/cryo pumps) to avoid any problems with carbon contamination. Heating of our chamber is accomplished with a combination of quartz lamps inside the chamber and external heating tapes. The electron beam source and quartz crystal thin film thickness monitor are water cooled. The pump down sequence for this chamber, which includes a bakeout, requires one and a half to two days. The chamber is illustrated schematically in figure 1.

A 7.5 cm diameter silicon substrate is attached to an adjustable sample holder which can be translated in three orthogonal directions and rotated about the plane of incidence for ellipsometry and reflectance measurements. The material in the shuttered e-beam source is evaporated onto the substrate with the film thickness controlled by a quartz crystal monitor.

3. Visible Ellipsometer

The in situ visible ellipsometer employed on our UHV chamber is a Gaertner model L104ALC, rotating analyzer, automated ellipsometer with a helium neon laser light source. The source and detector modules of the ellipsometer are located outside the UHV chamber and view the sample through fused silica windows. In order to avoid problems with stress and temperature induced birefringence in the fused silica windows, we utilized a differential measurement of the ellipsometric parameter delta. Thus, only changes in delta were used to calculate the change in surface oxide layer thickness.

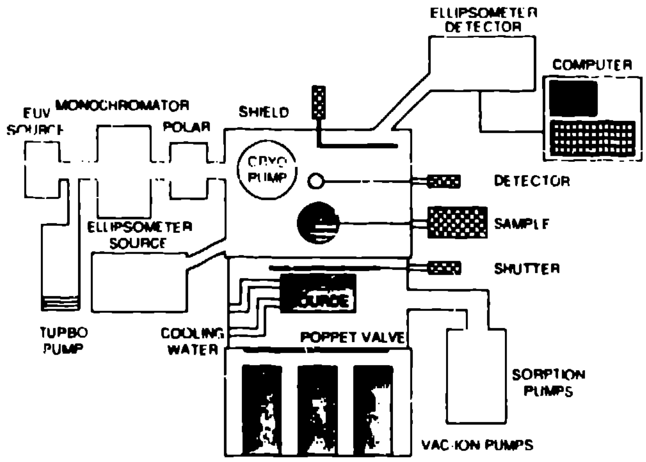

Figure 1. Schematic drawing of our UHV deposition and analysis system. All vacuum pumps are oil-free. The in situ visible ellipsometer and XUV reflectometer are used to measure the oxidation of freshly evaporated films.

3.1 Aluminum Film Oxide Layer

The growth of a monolayer of oxide on the surface of a thin film is adequately modeled by the time evolution of the fractional coverage parameter θ, given by

$$\frac{d\theta}{dt} = R*P*(1-\theta)^n \qquad (1)$$

where R is the rate constant, P is the pressure, n is the order parameter, and t is the time. The ellipsometer data for aluminum exposed to 2×10^{-8} Torr of oxygen is given in figure 2a and the solid curve is a fit of eq. (1) to this data. The value for R found from this fit is 2.89×10^{6} [monolayers/Torr*min]. In addition, we find that the order parameter n = 1, which implies that this is a first order reaction. Another set of data which was taken on aluminum exposed to 1×10^{-8} Torr of oxygen is given in figure 2b and the solid curve is calculated from eq. (1) with the rate constant and order parameter deduced from the previous experiment. The fit to the data in figure 2b is good, which indicates that the linear pressure dependence in eq. (1) is correct for this reaction. The measured rate constant for aluminum indicates a sticking coefficient of .05, which means that only 5 out of 100 oxygen molecules that strike the fresh aluminum surface "stick" to the surface.

A second set of ellipsometric experiments was performed on fresh aluminum exposed to water vapor instead of oxygen. The results of these experiments are indicated in figures 3a and 3b for water vapor pressures of 2×10^{-7} Torr and 1×10^{-7} Torr, respectively. These data also fit equation (1) using the same rate constant and order parameter that were obtained for the oxygen data. However, there is a time delay at the start of the reaction for water vapor. The time delay scales linearly with the pressure as can be seen from these two figures. This time delay may be caused by the formation of initial nucleation sites before the aluminum surface reaction can proceed.

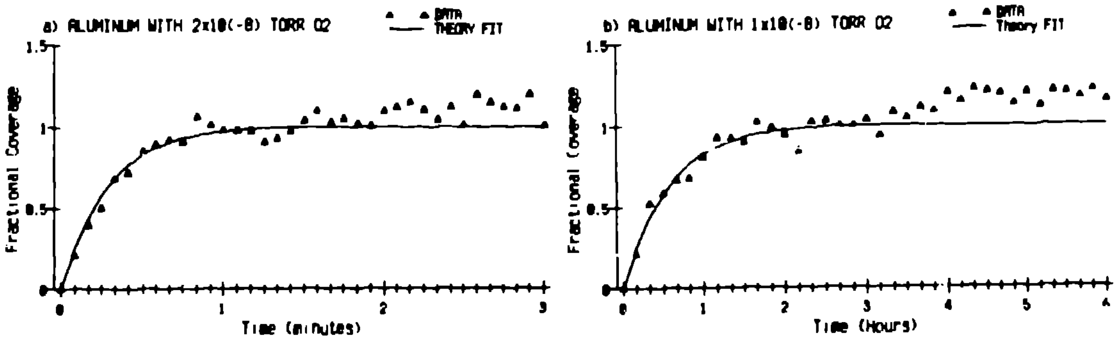

Figure 2. The growth of a monolayer of oxide on a freshly deposited aluminum film exposed to a) 2×10^{-8} Torr and b) 10^{-8} Torr of oxygen is shown in this ellipsometer data. The solid curves are calculated from a fit of eq. (1) to the data in a) and this fit yields the parameters given in the text.

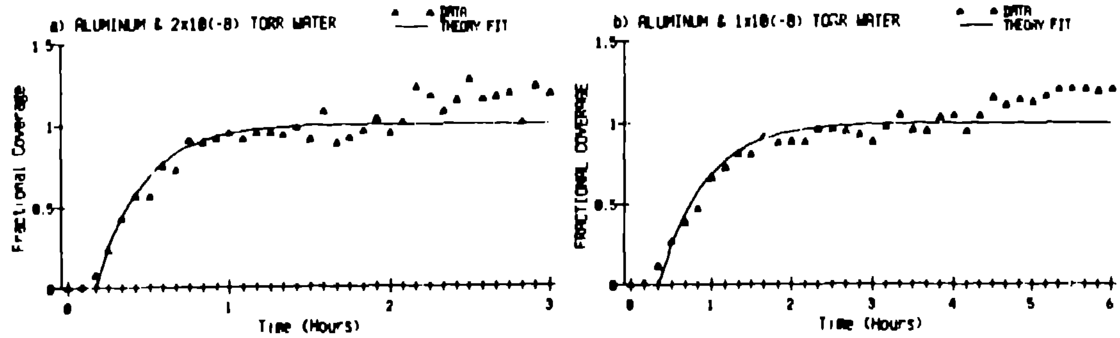

Figure 3. The growth of a monolayer of oxide on a freshly deposited aluminum film exposed to a) 2×10^{-8} Torr and b) 10^{-8} Torr of water vapor is shown in this ellipsometer data. The solid curves are calculated with eq. (1) using parameters fit to the data in figure 2a with the addition of a time delay at the beginning of the run.

3.2 Silicon Film Oxide Layer

We have evaporated silicon films onto specially prepared silicon substrates in a manner analagous to the experiments performed with aluminum. The special preparation of the substrates involved evaporating aluminum films, which were subsequently oxidized, onto the silicon substrates. Unlike aluminum, silicon is relatively transparent to the 632.8 nm HeNe ellipsometer source and this preparation was required to enhance the sensitivity of the ellipsometer to the formation of silicon oxide on the surface of freshly deposited silicon.

The results of our ellipsometer measurements of oxide growth on silicon are indicated in figures 4a and 4b for oxygen pressures of 1×10^{-7} Torr and 5×10^{-8} Torr, respectively. The indicated fit of eq. (1) to these data yields a rate constant $R = 6.3 \times 10^{7}$ [monolayers/Torr*min] and linear pressure dependence. The order parameter for the silicon/oxygen reaction is found to be 2, which indicates that this is a second order reaction.

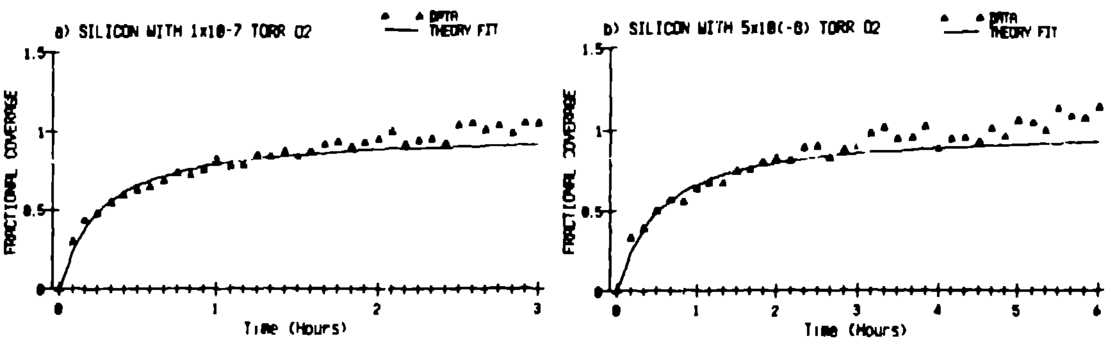

Figure 4. The growth of a monolayer of oxide on a freshly deposited silicon film exposed to a) 10^{-7} Torr and b)5 x 10^{-8} Torr of oxygen is shown in this ellipsometer data. The solid curves are calculated from a fit of eq. (1) to the data in a) and this fit yields the parameters given in the text.

4. XUV Reflectometer

The in situ XUV reflectometer, which is an integral part of our UHV vacuum chamber, consists of a capillary discharge source, a simple grating monochrometer, an imaging microchannel plate detector, and a sample holder with several degrees of freedom (our XUV polarizer was not used in these measurements). The detector and sample can be rotated about the plane of incidence in order to measure reflectance vs angle of incidence. The sample can also be positioned in x,y,z translations for proper alignment. There is no window between the gas discharge source and the UHV chamber due to the excessive absorption of XUV photons that would be caused by such a window. The error in our XUV reflectance measurements is estimated to be ±2% of the measured value.

4.1 Aluminum Film Reflectance

Reflectance vs angle of incidence measurements were performed on a freshly evaporated aluminum film at 58.4 nm in our UHV system. In addition, we exposed the sample to sufficient oxygen in our chamber to form a monolayer of surface oxide and we then remeasured the reflectance. Finally, we vented the chamber to air for about 35 minutes before pumping the chamber down again and remeasuring the reflectance. The results of these measurements are given in figure 5. The calculated curves in figure 5 utilized previously published optical constants for the oxides of silicon and aluminum [10,11]. The optical constants for the aluminum were fit to the reflectance data for the fresh aluminum film and then used in all three calculated curves. The optical constants derived from this analysis are given in table 1. The constants given in the column labeled "old" are from reference 10.

The reflectance data in figure 5 indicate that there is a strong total-external-reflectance (TER) effect in aluminum at 58.4 nm wavelength. In addition, this data indicates that a surface oxide layer has a very serious degrading effect on the XUV reflectance of aluminum films.

4.2 Silicon Film Reflectance

We measured the reflectance vs angle of incidence at 58.4 nm for a freshly deposited silicon film as shown in figure 6. We then performed surface oxidation and reflectance measurements on this silicon sample similar to those already described for aluminum. The optical constants of the oxide layers were obtained from published values as in the aluminum case [10,11]. The optical constants for silicon were obtained from a fit to the reflectance data from the freshly deposited film and these constants were used in the three calculated curves in figure 6. The optical constants obtained from this work are compared to previously published values in table 1.

The XUV reflectance of silicon shows a pronounced TER effect that is not quite as dramatic as that of aluminum due to the higher absorption of silicon (see k values in table 1). It is

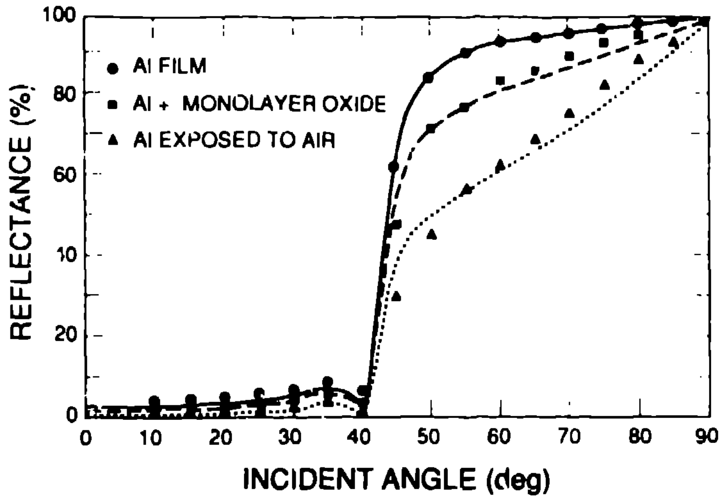

Figure 5. Reflectance vs angle of incidence for an aluminum film at 58.4 nm wavelength. The solid line is calculated for aluminum that is oxide-free (corresponding to the ● data). The dashed line is calculated for aluminum with one surface monolayer of oxide (corresponding to the ■ data). The dotted line is calculated for aluminum with three surface monolayers of oxide (corresponding to the ▲ data).

Table 1. Optical constants at 58.4 nm

Material		Old	This Work
Aluminum	n	0.715	0.700±0.005
	k	0.024	0.010±0.002
Silicon	n	0.637	0.637±0.005
	k	0.054	0.042±0.003

also evident from these reflectance measurements that the presence of surface oxide on silicon degrades the XUV reflectance but not as dramatically as the aluminum case.

5. Reflector Lifetime

The lifetime of a UHV aluminum reflector can also be evaluated with the XUV reflectance measurement outlined in this paper. In order to accomplish this measurement, we overcoated the oxidized aluminum sample with a fresh layer of aluminum in the UHV system. We measured the reflectance vs angle of incidence for this fresh film (indicated in figure 7) and then allowed the film to sit in the UHV chamber for 4 weeks. The pressure in the UHV chamber during this life test was greater than 2×10^{-9} Torr (mostly helium from our XUV source). After the four weeks of elapsed time, the reflectance was remeasured and this result is given in figure 7. We were very pleased to observe that the reflectance degradation during this life test was minimal.

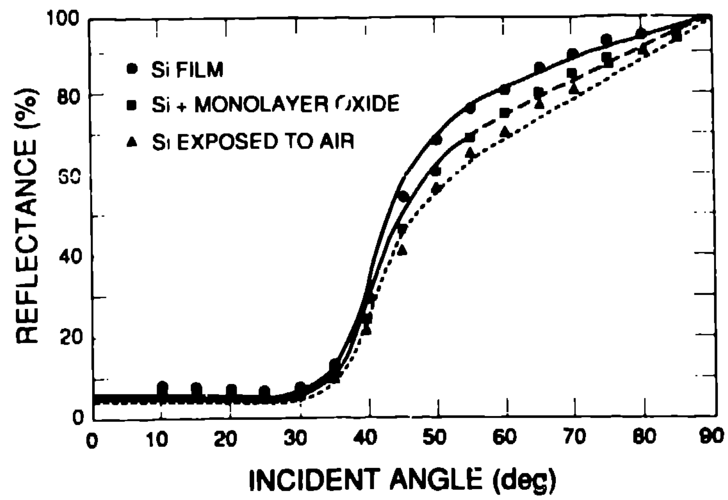

Figure 6. Reflectance vs angle of incidence data for a silicon film at 58.4 nm wavelength. The solid line is calculated for silicon that is oxide-free (corresponding to the ● data). The dashed line is calculated for silicon with one surface monolayer of oxide (corresponding to the ■ data). The dotted line is calculated for silicon with two surface monolayers of oxide (corresponding to the ▲ data).

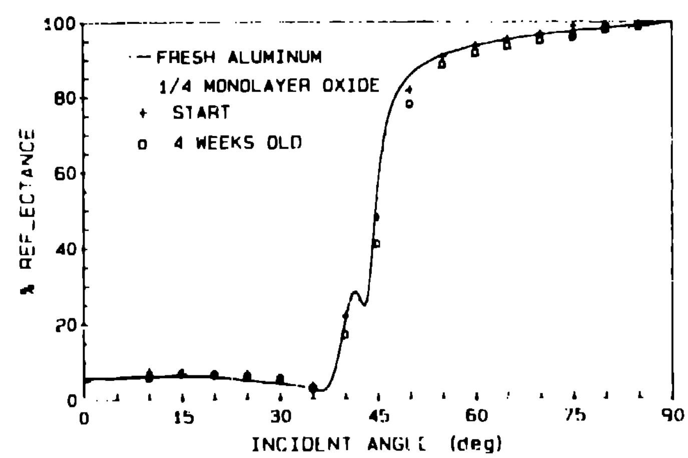

Figure 7. Reflectance vs angle of incidence for a fresh aluminum film overcoating a previously deposited and oxidized aluminum film (solid line and + data). This same film is measured again after four weeks in our UHV system at a helium pressure of 2×10^{-9} Torr or greater (dotted line and o data). The interference effect seen between 35° and 45° is due to subsurface reflections from the substrate and overcoated aluminum plus oxide layers.

6. Conclusions

The formation of surface oxides on aluminum and silicon films freshly deposited in an UHV system have been observed with visible ellipsometry. A monolayer of surface oxide forms on the aluminum when exposed to sufficient oxygen or water vapor with a sticking coefficient of .05 in each case. There is a significant time delay before the start of the formation of the oxide monolayer for water vapor, whereas there is no delay in the case of oxygen exposure. Similarly, a monolayer of surface oxide forms on fresh silicon, when exposed to a sufficient quantity of oxygen, with a .01 sticking coefficient. Silicon does not form an oxide in our UHV chamber when exposed to water vapor pressures as high as 10^{-4} Torr.

XUV reflectance vs angle of incidence measurements on aluminum and silicon films freshly evaporated in our UHV chamber and subsequently exposed to oxygen indicate substantial reductions in reflectance caused by the oxide. Optical constants determined by our measurements indicate lower absorption values for both aluminum and silicon than previously published values. The lower values of the absorption index k obtained in this study are probably due to the high purity of the starting material and the lack of any oxidation during the deposition in our UHV chamber.

A four week life test for an aluminum reflector indicated that minimal degradation of the reflectance occurs when the mirror is kept in an UHV system with minimal oxygen and water vapor partial pressures.

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